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Excitons and rare-earth ions in $CsCdBr_3$

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Abstract

$CsCdBr_3$ has a quasi-linear crystal structure. It consists of covalently bound $[CdBr]_6^{4-}$ chains separated by chains of Cs^+ ions. The trivalent rare-earth (RE) ions substitute for divalent Cd ions forming predominantly pair centers of the type RE^{3+}-(Cd vacancy)-RE^{3+}. A minority of RE ions forms "single-ion" centers with more distant charge compensation. The electronic structure around the band gap is determined by the $[CdBr]_6^{4-}$ octahedra. The lowest excitonic states of the lattice are charge-transfer states of these octahedra. At low temperatures they form self-trapped excitons which become mobile around 80 K.

In addition we find defect-localized excitons at the RE pairs and single ions with slightly modified spectra. There is a strong energy transfer between the RE ions and the defect-localized excitons in both directions with transition times below 10^{-8} s. For the cooperative fluorescence transition $^1D_2 \times {}^1G_4 \rightarrow {}^3H_4 \times {}^3H_4$ in Pr^{3+}: $CsCdBr_3$ a frequency-modulated vibronic sideband spectrum was found with up to four repetitions of the frequency of the localized optical phonon mode at the ion pair.

Keywords: Rare-earth ions; Excitons; $CsCdBr_3$

1. Introduction

$CsCdBr_3$ consists of chains of $[CdBr_6]^{4-}$ octahedra separated by parallel chains of Cs^+ ions. The Cd–Br bond is strongly covalent, whereas the Cs–Br bond is ionic. Both chains have the same trigonal basis so that the crystal easily tends to stacking faults. The trivalent rare-earth (RE) ions substitute for the divalent Cd^{2+} ions. For reasons of charge compensation and the quasi-linear crystal structure the majority of the RE ions forms pairs of the form RE^{3+}-(Cd-vacancy)-RE^{3+}. Only a minority of several percents forms centers with more distant charge compensation [1]. Because of the covalent bond in the Cd–Br chain, the RE pairs form strongly bound molecular complexes with their Br ligands. This leads to strong energy exchange between the RE ions and the excitonic states of the ligands [2], mixing of the 4f and ligand wave functions [3], and to the formation of localized lattice modes [3,4].

In this paper, we want to report about X-ray excited luminescence and thermoluminescence, optical excitation and emission spectra of the intrinsic and defect-localized excitons, thermal activation of the migration of the selftrapped intrinsic excitons and the resulting energy transfer to the RE centers, and about the cooperative emission $^1D_2 \times {}^1G_4 \rightarrow {}^3H_4 \times {}^3H_4$ of the Pr^{3+} pairs and its coherently modulated vibronic sideband spectrum due to the localized mode.

2. Results and discussion

Fig. 1 shows the X-ray excited fluorescence of pure $CsCdBr_3$ at different temperatures. X-ray excitation has the advantage of exciting the different centers of the crystal with about the same probability. The most intensive peak around 13,600 cm^{-1} obviously belongs to the regular lattice, while the shoulder around ~17,800 cm^{-1} belongs to minority centers. The violet emission band at 26,500 cm^{-1} with the two optical excitation bands at 31,600 and 32,200 cm^{-1} could not be found by X-ray excitation. It has been interpreted earlier as being characteristic for $CsCdBr_3$ [5,6]. It was found by us only by optical excitation and has been interpreted as the $e_g(\sigma^a) - t_{1u}(\sigma^a, \pi^a)$ [7] transition in quite rare "isolated" $[CdBr_6]^{4-}$ octahedra.

Fig. 2 shows the optical excitation and emission spectra. Three different spectra could be isolated. The spectrum of the intrinsic excitons has the highest excitation and lowest emission bands. The two other spectra were interpreted as

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